

PHYSICAL CHEMISTRY 3510

EXAM 2

October 21, 2013

*IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give the reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation. Give units for all quantities!*

Your name: SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

$$N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$dU = dq + dw$$

$$H = U + pV$$

$$dw = -p_{\text{ex}} dV$$

$$\gamma = C_p/C_v$$

$$\text{Perfect gas: } pV = nRT$$

$$C_p - C_v = nR$$

$$\text{Heat engine: } \varepsilon = (T_h - T_c)/T_h$$

$$\text{Adiabat: } pV^\gamma = \text{constant}$$

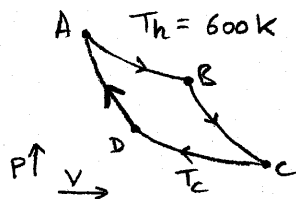
$$dS = dq_{\text{rev}}/T$$

$$G = H - TS$$

$$A = U - TS$$

1) 30 points

Consider the reversible Carnot cycle below, where the working fluid is 1 mol of perfect gas.



- When 40 J of heat is absorbed at  $T_h$ , 25 J of work are obtained. Calculate the efficiency and  $T_c$ .
- What can you say about the work obtained if the cycle was irreversible?
- What can you say about the sum of the changes in enthalpy for the four steps  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ , and why?
- What can you say about the heat transfer in the  $B \rightarrow C$  step?
- If the cycle was run in reverse and 10 J of work were done on the system, how much heat would be absorbed at  $T_c$ ?

a)  $\epsilon = \frac{25 \text{ J}}{40 \text{ J}} = 0.625 = \frac{T_h - T_c}{T_h} \therefore 375 \text{ K} = 600 \text{ K} - T_c \therefore T_c = 225 \text{ K}$ .

b) The work obtained would be less.

c) Because this is a cycle and the system returns to its original state, there is no net change in any state function, and  $\Delta H = \oint dH = 0$ .

d) Zero for an adiabatic change.

e) If run forwards,  $\epsilon = \frac{-w}{q_h} = \frac{10 \text{ J}}{16 \text{ J}} = 0.625 \therefore q_h = 16 \text{ J}$ .

Thus, when run in reverse, 16 J are rejected at  $T_h$ , 10 J come from the work, so  $q_c = 16 \text{ J} - 10 \text{ J} = 6 \text{ J}$ .

2) 30 points

Consider two blocks of aluminum (the system), one at 400 K and the other at 300 K. They are allowed to touch and 100 J of heat are transferred to the colder block. Calculate  $\Delta S$  for the system (*show work*). You may assume that the blocks have enough heat capacity that their temperatures remain constant.

This is a spontaneous process. We need to design a reversible path to the same final state.

i) Reversibly and isothermally transfer 100 J to gas in a piston (in the surroundings)

$$\Delta S_{\text{sys}} = \frac{-100 \text{ J}}{400 \text{ K}} = -0.25 \text{ JK}^{-1}$$

ii) Let the gas expand reversibly and adiabatically until its temperature drops to 300 K.  $\Delta S_{\text{sur}} = 0$  and  $\Delta S_{\text{sys}} = 0$  because  $q_{\text{rev}} = 0$ .

iii) Compress the gas reversibly and isothermally until 100 J are transferred to the cooler block:

$$\Delta S_{\text{sys}} = \frac{100 \text{ J}}{300 \text{ K}} \approx +0.333 \text{ JK}^{-1}$$

$$\text{Overall } \Delta S_{\text{sys}} = -0.25 + 0.333 \text{ JK}^{-1} = 0.083 \text{ JK}^{-1}$$

and because  $S$  is a state function, this is  $\Delta S$  for the original irreversible process too.

3) 40 points

i) Starting with an expression for  $dG$  in terms of  $p$ ,  $V$ ,  $T$  and  $S$ , show that

$$(\partial V / \partial T)_p = -(\partial S / \partial p)_T.$$

ii) Hence determine  $\Delta S$  for the isothermal expansion of 1 mole of a non-ideal gas accomplished by reducing the pressure from  $p_1$  to  $p_2$ . The equation of state for 1 mole of this gas is  $p = (RT/V) - a$ .

$$i) dU = dq + dw = Tds - pdv$$

$$\begin{aligned} G = H - TS = U + pV - TS \quad \therefore dG &= dU + Vdp + pdV - SdT - TdS \\ &= (\cancel{Tds} - \cancel{pdv}) + Vdp + pdV - SdT - TdS \\ &= Vdp - SdT. \end{aligned}$$

If  $G$  is  $G(p, T)$ , then  $dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$

The coefficients of  $dp$  and  $dT$  are equal in these formulations of  $dG$ ,

so  $\left(\frac{\partial G}{\partial p}\right)_T = V$  and  $\left(\frac{\partial G}{\partial T}\right)_p = -S$ .

The second derivatives are equal:

$$\frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p}\right)_T\right)_p = \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T}\right)_p\right)_T = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$ii) \Delta S = \int ds = \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p}\right)_T dp.$$

Here,  $p = \frac{RT}{V} - a \quad \therefore p+a = \frac{RT}{V} \quad \therefore V = \frac{RT}{p+a} \quad \therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p+a}$

$$\begin{aligned} \therefore \Delta S &= \int_{p_1}^{p_2} \frac{-R}{p+a} dp = -R [\ln(p+a)]_{p_1}^{p_2} = -R \ln \left(\frac{p_2+a}{p_1+a}\right) \\ &= R \ln \left(\frac{p_1+a}{p_2+a}\right). \end{aligned}$$